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DEVELOPMENT OF A MOLTEN CARBONATE PROCESS FOR REMOVAL OF SULFUR DIOXIDE FROM POWER PLANT STACK GASES

PROGRESS REPORT NUMBER 2
PART III. MATERIALS STUDIES
April 1, 1968 to October 27, 1968

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TABLE OF CONTENTS

		Page
	Summary	1
I.	Introduction	2
II.	Experimental Procedure	3
III.	Results	3
	A. Screening Tests (50 hr)	3
	1. 500°C	3
	2. 600°C	9
	3. 700°C	11
	B. Medium Term Tests (1500 hr)	11
	C. Long Term Tests (1 year)	13
	D. Special Tests	15
	1. Thermal Cycle Tests	15
	2. Thermal Convection Loop Tests	15
	3. Selective Leaching	17
	4. Passivated Films	19
IV.	Discussion	21
V.	Recommended Material for Small Pilot Plant	23
	A. Absorption and Regeneration	23
	B. Reduction	23
	C. Back-Up Materials	24
VI.	Future Corrosion Test Program	24
VII.	Conclusions	25
VIII.	References	26

FIGURES

Figure 1.	Static Corrosion Test Apparatus	4
Figure 2.	Dynamic Corrosion Test Vessel	5

TABLES

Table I	Composition of Materials and Static Corrosion Rates in Process Melts at 500 °C for 50 hours	6
Table II	Fifty Hour, Static Corrosion Rates of Materials in Process Melts at 600°C	10

TABLE OF CONTENTS (Cont'd.)

TABLES (cont'd)

Table III	Fifty Hour, Static Corrosion Rates of Materials in Process Melts at 700°C . .	12
Table IV	Fifteen Hundred Hour Dynamic Corrosion Tests . . .	14
Table V	Effect of Thermal Cycling on Corrosion Rate at 600°C in Sulfite Melts . .	16
Table VI	Selective Leaching of Alloying Constituents from Various Materials . . .	18
Table VII	Relative Content of Metals in the Passivated Film Found on Haynes 25 and Uniloy . . .	20

SUMMARY

The molten alkali carbonate eutectic consists of essentially equal parts by weight of lithium, sodium and potassium carbonate. It may be used to control SO_2 air pollution by scrubbing stack gases with the molten salt. The resultant fused salt contains sulfite which disproportionates to sulfate and sulfide. Suitable containment of these molten salts in H_2O, CO_2, and H_2S gaseous environments is required for commercial development of this technique to control air pollution. The results of screening, medium-term and long-term static, dynamic, and thermal cycle tests are given. At 500°C, SS 347 appears to contain all of the above melts satisfactorily. At 600°C, satisfactory containment of the melts with sulfur compounds present required low-iron, nickel- or cobalt-based alloys with about a 20% chromium content, while SS 347 satisfactorily contains the pure carbonate melt. At higher temperatures, containment of these melts requires high-chromium alloys, ceramics, cermets, or a frozen skull of the salt. Materials for the Small Pilot Plant are recommended and the future corrosion program is outlined.

I. INTRODUCTION

Molten alkali metal carbonate eutectic,[1] consisting of approximately equal weights of Li_2CO_3, Na_2CO_3 and K_2CO_3, is an excellent absorbent of SO_2[2,3] above its melting point. The eutectic freezing point of 395°C is depressed to a lower temperature when sulfur compounds are present in the melt. Since this melt is stable against decomposition even at much higher temperatures,[4,5] it is being used as the absorbant in the molten carbonate process to remove sulfur oxides from stack gases. However, commercial utilization of this process requires corrosion resistant materials. Therefore, an extensive program was undertaken to determine which materials would suitably contain the process melts.

The program consisted of short-term (50 hr) static screening tests, medium-term (1500 hr) dynamic tests of the more promising materials, and long-term (1 yr) dynamic tests of the most promising materials. Preliminary tests indicated that sulfide was more corrosive than sulfite at 500°C. Therefore, most of the screening tests were run in pure carbonate melts and in carbonate-20% sulfide melts. Later tests at higher temperatures indicated that sulfite was more corrosive than sulfide; therefore, a number of high temperature medium-term tests were run in carbonate-20% sulfite melts. Initially screening tests were made at 500°C and these were followed by tests at 600°, 700°C and higher if the material warranted. Most of the screening tests were completed during the first report period; results of these tests are included for comparison and completeness.

Special corrosion tests were also done to study the effects of thermal cycling and circulation within a thermal gradient loop.

II. EXPERIMENTAL PROCEDURE

Corrosion data in the literature[6] indicated the SS 347 would suitably contain the alkali metal carbonate eutectic near its melting point. Thus all short term tests at 500°C were made in SS 347 vessels. The corrosion specimens were suspended from a jig as shown in Fig. 1. Silica or alumina insulators prevented electrolytic contact between specimens and vessel walls. In general four different specimens (only two are shown in Fig. 1) of the same material were tested at one time.

The dynamic test vessel is shown in Fig. 2. Again four specimens per test were used. However, since insulators could not be used to prevent electrical contact between specimens and vessel walls, the vessel itself was constructed of the material under test or an alumina crucible and jig were used to prevent specimen-vessel contact. The vessels were inclined at an angle of 20° from horizontal (note melt level in Fig. 2) and rotated at 23 rpm. In this manner salt constantly flowed over the specimen surfaces.

III. RESULTS

A. Screening Tests (50 hour)

1) 500°C Results of the 50-hr. screening tests in carbonate and carbonate-sulfide melts at 500°C are given in Table I. Along with the corrosion rates in $mg/cm^2/hr$ are the nominal alloy composition. The results in Table I are grouped into four general categories: (1) iron-based materials, (2) nickel (cobalt)-based materials, (3) other metals, and (4) nonmetals. In general, the melt was more corrosive than the vapor. The rates reported in all tables are based upon the total specimen area only about half of which was exposed to the melt.

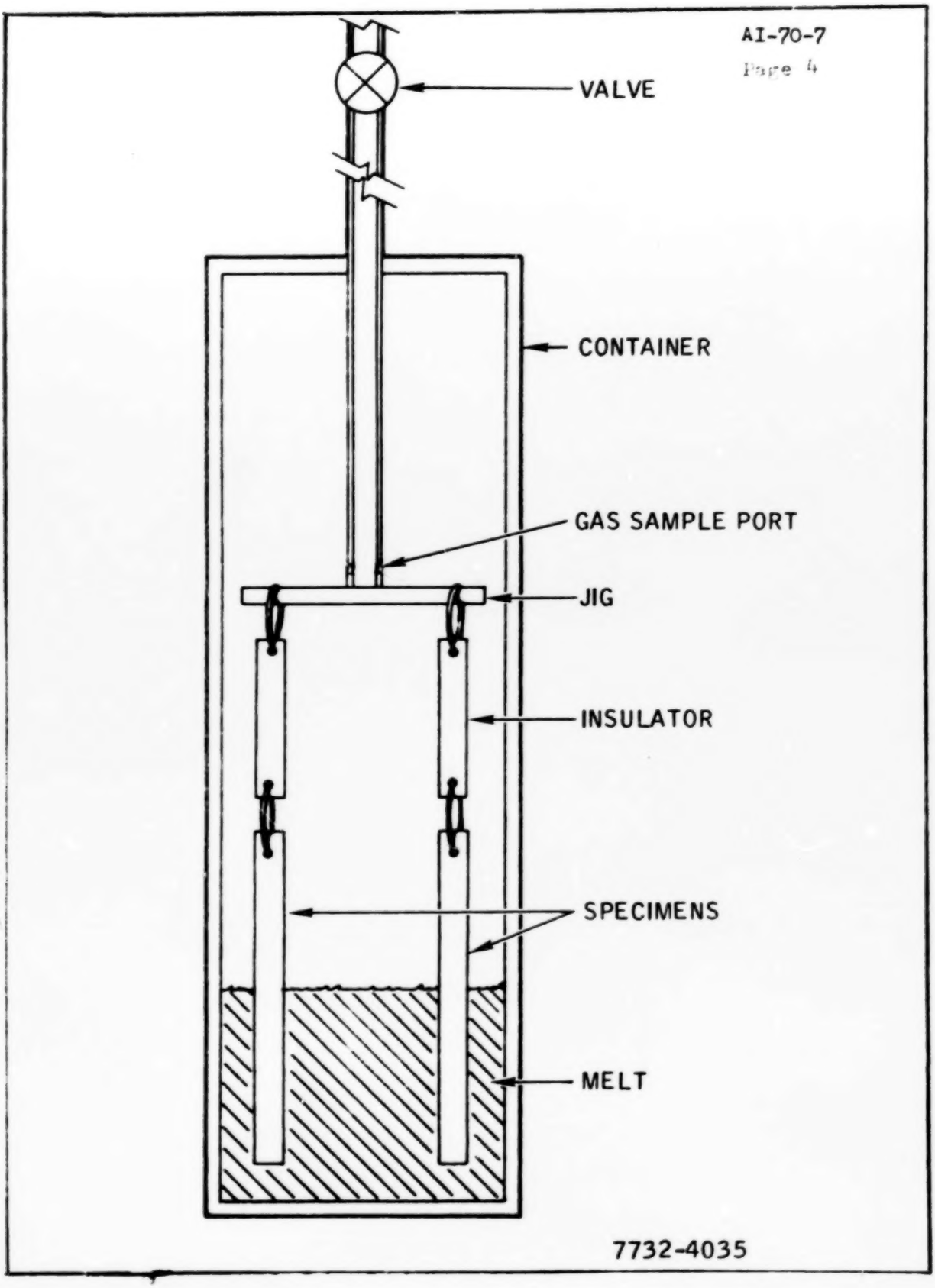

FIGURE 1. STATIC CORROSION TEST APPARATUS

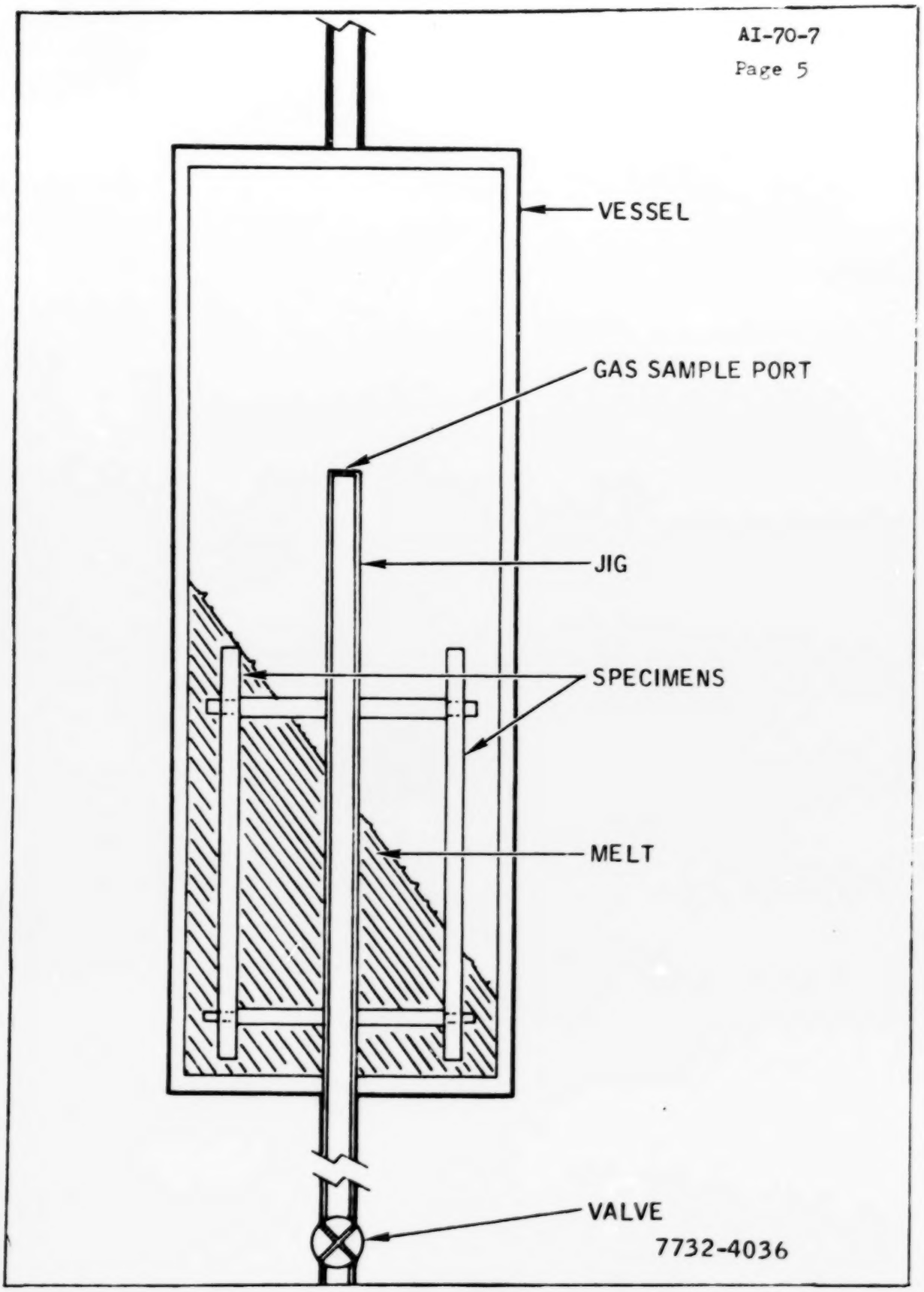

FIGURE 2. DYNAMIC CORROSION TEST VESSEL

TABLE I

Composition of Materials and Static Corrosion R tes in Process Melts at 500°C for 50 Hours

Material	Corrosion Rate ($mg/cm^2/hr$)[a]		Nominal Alloy Composition (wt %)						
	$CO_3^=$	20% $S^=$	Fe	Ni	Cr	C[b]	Mn[b]	Si[b]	Other
*Armco-5	.0096	.65 I	99+			.012	.017		
*1020 steel	.011	.63 I	99			0.23	.5		
SS 304	.013 I	.49 I	68	10	19	.08	2	1	
*SS 304 L	.0011	.25	68	10	19	.03	2	1	
*SS 310	.0009	.20	51	21	25	.25	2	1.5	
SS 316	.011 I	.47 I	66	12	17	.08	2	1	MO 2
SS 321	.014	.54	68	10	18	.08	2	1	Ti .4
*SS 347[c]	.015	.66	67	11	18	.08	2	1	Nb 1
SS 405	-.008 I	.75 I	87		13	.08	1	1	
SS 410	.013 I	.49 I	87		13	.15	1	1	
SS 430	.0065	.54 P	84		16	.12	1	1	
SS 446	.0014 I	.67 I	75		25	.20	1.5	1	
Carpenter 20	-.0005	.13	36	34	20	.07	2	1	Mo 2.5, Cu 3.5, Nb 1
*Multimet	.0007	.019	30	20	21	.25	1.5	1	Co 20, Mo 3, W 2.5, Nb+Ta 1,
Nickel 200	-.0019 I	.45 I	.15	99.5		.06	.25	.05	Cu .05
Nickel 201	-.0013 I	.47 I	.15	99.5		.02	.2	.05	Cu .05
Inconel 600	-.0001	.22	8	76	16	.08	.5	.25	Cu .25
Inconel 702	-.0002	.14	1	79.5	16	.05	.5	.35	Al 3.4, Ti .7
Hastelloy B	-.0041	.17 I	5	61	1	.05	1	1	Co 2.5, Mo 28, V .4
Hastelloy C	-.0002	.35 P	5.5	54	15.5	.08	1	1	Co 2.5, Mo 16, W 3.6, V .4
*Hastelloy G	-.0005	.016	20	44	22				Co 2.5, Mo 6.5, W 1, Cu 2, Nb 2
*Hastelloy N	.0005 I	.076 I	5	69.5	7	.06	.8		Mo 17, W .6, Al .5
*Hastelloy X	-.0009	.080	18.5	47	22	.1	1	1	Co 1.5, Mo 9, W .6
Monel 400	.000 I	.28 I	1	66		.15	1	.25	Cu 32
Monel K 500	-.0001 I	.15 I	1	66		.13	1	.5	Ti .6, Cu 30, Al 3
Tophet A	.0009 P	.17		80	20				
*Haynes 25	.0011	.0032	3	10	20				Co 52, W 15

* Data from previous report period

TABLE I (Continued)

Composition of Materials and Static Corrosion Rates in Process Melts at 500°C for 50 Hours

Material	Corrosion Rate ($mg/cm^2/hr$)[a]		Nominal Alloy Composition (wt %)						
	$CO_3^=$	20% $S^=$	Fe	Ni	Cr	C	Mn	Si	Other
Palladium-Gold	.0002	.27	–	–	–	–	–	–	Pd 80, Au 20
Gold	.0021	2.3 I	–	–	–	–	–	–	
Niobium	.068	.27	–	–	–	–	–	–	
*Tantalum	-.07	.001	–	–	–	–	–	–	
Zirconium	-.008	-.08	–	–	–	–	–	–	
Zircalloy II	-.005	-.005	–	–	–	–	–	–	Zr 98, Sn 2
Vanadium	.025	.026	–	–	–	–	–	–	
*Titanium	.0000	.0000	–	–	–	–	–	–	
*Graphite[d]	.003	.002 P	–	–	–	–	–	–	
*Graphite[e]	.002 P	.003	–	–	–	–	–	–	
*Graphite[f]	.17	.13	–	–	–	–	–	–	
*Graphite[g]	.007	-.4[h]	–	–	–	–	–	–	
*Zirconia	-.4[h]	-.4[h]	–	–	–	–	–	–	
*Magnesia	-.8[h]	-.9[h]	–	–	–	–	–	–	
*Alumina	-.0002[h]	.0001	–	–	–	–	–	–	
Silica	.11	.21	–	–	–	–	–	–	

a) General surface corrosion unless specified by symbol. I & P refer to intergranular and pitting corrosion respectively. A negative sign indicates a weight gain during the test; the corrosion rate for these tests was calculated from the weight increase assuming that the weight gain was due to oxide formation.

b) Maximum concentration for iron-based alloys; nominal concentration for other alloys.

c) The corrosion rate in sulfite was 0.13 $mg/cm^2/hr$.

d) AGSX graphite # 571X.

e) Carborundum Metal Pumping Service graphite

f) K.B. Bonite graphite.

g) Raschig ring 571 B

h) Weight gain due to melt absorption; corrosion rate is actually melt absorption rate.

* Data from previous report period

These screening test results clearly show that carbonate melts containing sulfide are in general orders of magnitude more corrosive than pure carbonate melts. These tests also show that the nickel-based alloys are much more corrosion-resistant to both melts than are the iron-based materials. In general the nonmetals have about the same corrosion resistance to both melts as is the case with several of the more refractory metals.

Even though carbon is a minor constituent in many of the alloys it appears to play a major role in corrosion of ferrous alloys particularly where intergranular corrosion was detected. SS 304L is low-carbon SS 304 but has a much lower corrosion rate in both melts. No evidence of intergranular attack was found in the 304 L specimens but was found in 304 specimens.

The metals, Ta, Zr, V and Ti are remarkably corrosion resistant to both melts. However, the cost, the difficulty in component fabrication and in some cases the instability of their oxides towards hydrogen and/or steam limit their usefulness in the molten carbonate process. Therefore these materials will not be examined further unless more easily fabricated materials prove unsatisfactory as containers.

Gold is very severely attacked by the melt containing sulfide but is fairly corrosion resistant to pure carbonate melts. The gold-palladium alloy (20 wt% Au) is an order of magnitude more corrosion resistant than pure gold.

The nonmetals (except silica) were quite corrosion resistant. Some brands of graphite were more corrosion resistant than other; pitting was detected in some graphite specimens. Zirconia and magnesia gained weight probably due to the absorption of the melt into the porous structure of these materials. Therefore actual corrosion rates could not be obtained from weight difference.

Corrosion rates in $mg/cm^2/hr$ (Table I) can be converted to the more meaningful mils/yr by multiplying by 440 (for materials such as Fe and Ni with specific gravities of about 8). It should be cautioned that the annual value in mils/yr is a linear extrapolation from 50 hours and in general corrosion is not a linear function of time. Yearly corrosion rates obtained in this manner from 50 hr tests may be an order of magnitude too high.

2) 600°C Fifty-hr. screening tests at 600°C were made on the materials that were corrosion resistant at 500°C. The results of these tests are given in Table II. Again it was found that melts containing sulfide are more corrosive than pure carbonate melts and that iron-based materials are corroded more severely than nickel- or cobalt-based alloys. All of the ceramics gained weight due to melt absorption; the corrosion rates given for these materials are actually melt absorption rates. All three of the ceramics listed were very corrosion-resistant.

The coated specimens were samples of 1020 steel substrate flame-sprayed (~5 mil) with the specified coating. This substrate was chosen so that massive corrosion would occur if the film were not continuous or protective. No effort was made to match the coefficients of thermal expansion of the substrate and coating. Thus it was not surprising that two of the films that were protective (i.e. Cr and Al_2O_3) spalled when cooled and mechanically shocked. The third protective coating (Cr-23% Al_2O_3) spalled when the substrate was bent several times. In the alumina and the Cr-Al_2O_3 coated specimens it was found that the alumina was present primarily as amorphous material while the alumina used in fabrication of vessels is α-alumina.

TABLE II

Fifty Hour, Static Corrosion Rates of Materials
in Process Melts at 600°C

Material	Corrosion Rate ($mg/cm^2/hr$)[a]	
	$CO_3^=$	20% $S^=$
SS 304 L	-.01	.92
SS 310	.011	.42
SS 347	.0055	1.0 I
*Multimet	.0049 I	.072 I
Inconel 600	-.002	.57
Inconel 702	-.009	.62
Hastelloy C	.0005	.90
*Hastelloy G	-.01	.040
Hastelloy N	.0011	1.1
*Hastelloy X	.008	.098
*Haynes 25	.004	.020
Zirconia	-.4[b]	-.5[b]
Magnesia	-.0002[b]	-.6[b]
Alumina	-.6[b]	-.0002[b]
Coatings[c]		
Ni-Cr	--	U
Cr	--	E, S
Alumina	--	E, S
Cr-Al_2O_3	--	E

a) I, U, E & S refer to Intergranular corrosion, Unsatisfactory, Excellent and Spalled-off respectively. A negative sign indicates a weight gain during the test; the corrosion rate for these tests was calculated from the weight increase assuming that the weight gain was due to oxide formation.

b) Weight gain due to melt absorption; corrosion rate is actually melt absorption rate.

c) Coating on 1020 steel substrate.

* Data from previous report period

Amorphous alumina slowly dissolved in carbonate-based melts while α-alumina did not. Most of the alumina in the Cr-Al_2O_3 coated specimen had dissolved where the melt contacted the specimens and at the conclusion of the tests the surface of the coating material was virtually pure chromium. Thus, amorphous alumina is not corrosion-resistant but the crystalline α-alumina is; this could be very important in applications.

3) 700°C The results of 50-hr. static corrosion tests at 700°C are given in Table III. The carbonate melt containing sulfide is much more corrosive than pure carbonate for iron-based material. The nickel- and chromium-based alloys and the metal oxides were not tested in pure carbonate since these conditions would not prevail in the plant. These results show that in sulfide melts the nickel-based alloys are more corrosion-resistant than the iron-based alloys and that the chromium-based alloys are much more corrosion resistant than the nickel-based alloys. These tests clearly show that high chromium content alloys are required to provide corrosion resistance at temperatures of 700°C and above in melts containing sulfur compounds; this was expected from results of published corrosion studies.[7] Several metal oxides also appear to be corrosion-resistant under these conditions. Perhaps the most easily fabricated high-chromium alloy is Uniloy. This alloy has shown remarkable corrosion resistance in Kraft Paper Process plants where similar melts and conditions prevail.[8,9,10]

B. Medium-Term Test (1500 hours)

The corrosion rates obtained from 1500-hr. dynamic tests of the more promising materials are given in Table IV. The effect of temperature and melt composition can be seen from the data in this table. At 500°C, the

TABLE III

Fifty Hour, Static Corrosion Rates of Materials
in Process Melts at 700°C

Material	Corrosion Rate ($mg/cm^2/hr$)		
	$CO_3^=$	20% $S^=$	20% $SO_3^=$
*SS 310	--	11.5	--
*SS 347	-.007[a]	.23	--
*Carpenter 20	.287	5.3(.4)[b]	--
*Multimet	.012	4.2(.2)[b]	--
*Hastelloy G	--	.90 (7.9)[b]	--
Hastelloy N	--	3.1	--
*Hastelloy X	--	.66	--
*Haynes 25	--	.73	--
Uniloy[c]	--	--	0.16
LT-1[d]	--	.018	--
Chromium	--	-.2[e]	--
Zirconia	--	E[e]	--
Alumina	--	E[e]	--
Magnesia	--	E[e]	--
Mullite[f]	--	E[e]	--
Porcelain[g]	--	E[e]	--

a) Corrosion rate calculated with the assumption that the weight increase is due to oxide formation.

b) Values in parenthesis are for experiments where an electrolytic short occurred in the insulation between the metal specimens being tested and a 347 vessel. Although these values are in error they are reported to illustrate the relative anodic-cathodic potential of the metal.

c) Uniloy; Cr 50%, Ni 49%, Ti 1%.

d) LT-1; Cr 77%, Al_2O_3 23%.

e) Weight increase due primarily to melt absorption in samples; E stands for Excellent corrosion resistance.

f) Mullite; $3Al_2O_3 \cdot SiO_2$.

g) Porcelain is Mullite with a silica glaze.

* Data from previous report period

sulfide melt appears to be the more corrosive of the three while at 600°C or above the sulfite is the more corrosive. Therefore, at higher temperatures most of the tests reported in Table IV were made with melts containing 20% sulfite.

The data in Table IV suggest that pure carbonates can be satisfactorily contained by SS 347 even at 600°C. Although SS 347 will probably contain all of the melts satisfactorily at 500°C, nickel or probably cobalt-based alloys[11] will be required to contain the sulfur-containing melts at 600°C temperature. At temperatures of 700°C or above chromium-based materials will be required to contain the melts. The ceramic, α-alumina, seems to contain all three melts at all three temperatures satisfactorily.

Large variation in the corrosion rates of several Uniloy specimens in the same tests and between the specimens and the Uniloy vessel in the same test were observed; such large variation in corrosion rate may have been due to non-uniformity of the Uniloy sheet stock. The corrosion rates (based on weight lost) were generally less than 10 mils/yr. However, severe vapor phase pitting with a pitting factor as high as 100 was observed in some vessels; this may also have been the result of non-uniform sheet stock. Corrosion at manual welds in Uniloy was particularly a problem.

C. Long-Term Test (1 year)

One long-term test has been completed to date, SS 347 in pure carbonate at 500°C. This dynamic test ran for a period of one year. The results of this test are reported in Table IV and indicate that SS 347 is very corrosion-resistant under these conditions.

TABLE IV

Fifteen Hundred-Hour Dynamic Corrosion Tests

Material	Temp. (°C)	Corrosion Rate (mils/yr)		
		CO_3	20% $S^=$	20% $SO_3^=$
SS 347	500	0.2[a]	14	9[b]
SS 347	600	0.3	50	> 90
SS 347	700	> 90	--	--
Hastelloy G	600	—	0	10
Hastelloy G	700	--	> 360	> 360
Hastelloy X	600	--	--	100
Hastelloy X	700	--	--	> 180
Haynes 25	600	--	--	2
Haynes 25[c]	650	--	3	7
Haynes 25	700	--	--	32
Uniloy[d]	700	0.5 - 3[e]	0.2 - 11	1 - 5
Uniloy[d]	800	--	--	1
LT-1	700	--	--	< 0.1
LT-1	890	--	--	< 0.6
Alumina	700	--	--	0.05
Alumina	890	--	--	0.3

a) One year test

b) The corrosion rate in sulfite melt under 50 psig water vapor was slightly less (8 mils/yr).

c) Corrosion rate of stressed specimens was 3 mils/yr in sulfide and 12 mils/yr in 20% sulfite.

d) Vapor phase pitting was observed.

e) 20% $SO_4^=$ melt.

D. Special Tests

1) Thermal Cycle Tests

If the passivated film which inhibits corrosion were to separate from the substrate during thermal cycles, the corrosion rate should be greater than that found in constant temperature tests. Since some thermal cycling may occur in the plant due to shutdown, it is important to determine if this would increase corrosion. Therefore corrosion tests of Haynes 25, Hastelloy G and X were made in molten carbonate-20% sulfite melts where the temperature was cycled daily (except weekends) from ambient to 600°C until 300, 1000 and 1500 hr respectively at temperatures above 575°C had elapsed. During these tests the average time elapsed per cycle was 20, 25 and 25 hr. respectively (i.e. 15, 40 and 40 cycles). The results of these corrosion tests are given in Table V together with those of 1500-hr. dynamic tests at 600°C in $CO_3^=$-20% $SO_3^=$ melts. These results show that the corrosion rates in the thermal cycle tests are 5 to 20 times those in the dynamic tests. Therefore it appears as if 2-3 thermal cycles (600°-ambient) will double the low corrosion rate predicted by the dynamic tests.

2) Thermal Convection Loop Tests

If the concentration of corrosion products in the melt influences the corrosion rate and if the solubility of these corrosion products varies with temperature, the corrosion rate in systems operating at two or more temperatures may be greater than that predicted from tests at constant temperatures. Since portions of the proposed molten carbonate process operate at different temperatures, it is important to determine if enhanced corrosion might be expected in thermal convection loops.

TABLE V

Effect of Thermal Cycling on Corrosion Rate at 600°C in Sulfite Melts

Material	Corrosion Rate (mils/yr)		Corrosion Rate Ratio	Cycles to Double Rate
	Thermal Cycle	Dynamic[a]		
Haynes 25	10[b]	2	5	3
Hastelloy G	200[c]	10	20	2
Hastelloy X	> 1700[c]	100	> 17	< 2 - 1/2

a) based on 1500-hr. dynamic tests without thermal cycles.

b) based on 300-hr. at temperatures above 575°C, 15 cycles.

c) based on 1000-hr. at temperatures above 575°C, 40 cycles.

A thermal loop test on Haynes 25 operating between 600°C and 450°C is in progress. A previous test loop constructed from Inconel 713 corroded through at the welds before the test was operated long enough to determine if thermal transport of alloying constituents had been transported from one temperature zone to another. Thermodynamic calculations indicate that if chromium is transported from the hot zone to the cold zone in the process it must be transported as an oxidized species. The oxidation potential of the alkali metal carbonates is such that even in highly reducing atmospheres the carbonate will keep chromium in the oxidized state. In other words the carbonate melt will be reduced before the chromium oxide passivated film will be attacked.

3) Selective Leaching

Removal of alloying constituents from the substrate at different rates, i.e. selective leaching, may alter long-term corrosion rates based on short-term tests. Therefore it is important to determine if selective leaching occurs in the metals being considered in the plant. Table VI gives the selective leaching of SS 347, Hastelloy G and Haynes 25 that occurred in three melts under different conditions. The selective leaching values given in Table VI are the relative concentration of alloying constituents in the melt divided by the weight percent of each constituent in the substrate. Therefore, if uniform corrosion had occurred all of the values in Table VI would have been unity. These results suggest that selective leaching may (1) be more pronounced in short-term tests than in long-term tests, (2) be more pronounced in carbonate melts (lower corrosion) than in other process melts, (3) not be significantly different in the two sulfur containing melts, and (4) not be more severe at higher temperature.

TABLE VI

Selective Leaching of Alloying Constituents from Various Materials[b]

Material and Test Conditions	Alloying Constituents	Nominal Composition (%)	Selective Leaching (a)			
			Carbonate Melts		1000 hr Dynamic	
			412 hr	8700 hr	20% $S^{=}$	20% $SO_3^{=}$
SS 347 at 500°C	Fe	67	2000	10	1	2
	Cr	18	1	1	1	1
	Ni	11	4	2	2	2
	Mn	2	200	20	3	1
	Nb	1	200	20	1	1
	Si	1	100	--	2	2
			Cycle Test 1500 hr		Dynamic Test 1500 hr	
Hastelloy G at 600°C in 20% $SO_3^{=}$ melts	Ni	44	1		1	
	Cr	22	2		2	
	Fe	20	10		4	
	Mo	6.5	5		10	
	Co	2.5	1		2	
	Nb	2	1		4	
	Cu	2	3		6	
			Cycle Test 300 hr at 600°C		Dynamic Tests 1500 hr	
					600°C	700°C
Haynes-25 in 20% $SO_3^{=}$ melts	Co	50	1		1	1
	Cr	20	1		1	3
	W	15	3		1	-
	Ni	10	2		10	2
	Fe	3	300		2	2
	Mn	1.5	30		3	-
	Si	1	80		5	-

a) These values are the relative concentrations of alloying constituents in the melt divided by the weight percent of each constituent in the substrate.
b) All percentages are weight %.

4) Passivated Films

X-ray diffraction and x-ray fluorescence techniques were used to identify the passivated film on nickel based specimens. The diffraction pattern and line intensities observed are the same as those listed for $LiNiO_2$ in the ASTM x-ray powder data file. $LiNiO_2$ has the CsCl rhombohedral structure as do many other materials such as $LiFeO_2$, $LiCoO_2$, $LiCrO_2$, etc.; thus it would be expected that all of these materials would have similar powder patterns.[12,13] Therefore, x-ray fluorescence was used to identify the particular trivalent cation present.

The passivated film was held so tenaciously to the metal substrate that it was impossible to obtain a pure sample of the film by mechanical means. X-ray fluorescence of the film on the substrate (x-rays also penetrate into the substrate to some extent) indicated that the chromium content of the film was much higher than that of the substrate and that the nickel content of the film was much less than that of the substrate. Less interference from the substrate was obtained by coating the film with Krylon on one side and then electrolyzing the metal away in aqueous acid solution, leaving the Krylon coated film nearly free of substrate. This was done for a Haynes-25 specimen. Results of x-ray fluorescence on this sample indicated that essentially no nickel was in the film. These results are summarized in Table VII and clearly show that the ratio of chromium to nickel is much greater in the film than in the substrate. Emission spectroscopy was used to determine that the relative concentration of the lithium, sodium, and potassium ions in the film, was approximately 5000:5:1.

TABLE VII

Relative Content of Metals in the Passivated Film Found on Haynes 25 and Uniloy

Alloy	Element	Relative Concentration (wt %)		
		Substrate	Film + Substrate	Film Free of Substrate[a]
Haynes 25	Ni	10	3	0.5
	W	15	23	30
	Cr	20	61	68
	Co	50	13	1.5
Uniloy	Ni	50	15	--[b]
	Cr	50	85	--[b]

a) Prepared by aqueous electrolysis; the true values for Co and Ni may be even less.

b) Analysis not completed.

IV. DISCUSSION

The reason the $LiCrO_2$ film is so protective is probably related to the compactness and tenacity of this material. If it is assumed that the oxygen ion determines the lattice parameters, the interstices can accomodate ions with radii of approximately 0.6 Å. The only ions which can be accomodated without lattice distortion [14] are Li^+, Cr^{+3}, Mo^{+4}, and W^{+4}. The divalent ions of iron, cobalt, and nickel are too large, [14] and the trivalent ions of these elements are thermodynamically unstable with respect to the divalent ions at the test temperatures. Both Na^+ and K^+, are too large [14] and are not found in the film. It should be noted that tungsten was found in Haynes 25 film (Table VII) as predicted from the size relationships.

The presence of the $LiCrO_2$ films suggests a possible mechanism of corrosion. The anodic reaction may be the dissolution of metal where no film is present or where the film is thinnest. (This may be the reason more corrosion is often found at the interface where the film is thinner than where the metal is completely exposed to the melt.) After the oxide layer forms at the interface, then the anodic reaction probably would be controlled by the diffusion of the metals through the film. The cathodic reaction may be the reduction of the sulfate, sulfite, or carbonate ions, and is probably controlled by electron conduction through the film. (The alternate mechanism of oxygen atom diffusion through the film to the substrate is probably not important due to the expected low concentration of oxygen in the process melts, particularly in a hydrogen or carbon reducing atmosphere.)

If the mechanism proposed above is correct, then the corrosion rate should be diffusion controlled and a parabolic rate should be observed. Indeed a marked decrease in corrosion rate with time was observed (characteristic of diffusion-controlled corrosion) as indicated by the extrapolated corrosion rates for SS 347 in carbonate melts at 500°C of 7, 3, and 0.2 mils/yr based on 50 hr, 412 hr and 1 year tests respectively or by the extrapolated corrosion rate of Haynes 25 in process melts containing sulfur compounds at 600°C of 9 and 2 mils/yr based on 50 and 1500 hr tests. Thus, the actual corrosion found in the plant will probably be much less than that predicted on the basis of the 1500 hr or even the 1 yr tests.

A summary of the linearly extrapolated corrosion rates of some of the more corrosion resistant materials is given in Table IV. As indicated previously, it is anticipated that the actual yearly corrosion rates will be considerably less than the rates calculated from 1500 hr tests. The results in Table IV show that at temperatures below 500°C the niobium-stabilized stainless steel 347 has a linearly extrapolated corrosion rate of only a few mils/yr even in the most corrosive (sulfide) fused salt. At higher temperatures (600 - 650°C) the cobalt-based alloy Haynes 25 is satisfactorily corrosion-resistant. At even higher temperatures (700°C) Uniloy is corrosion-resistant (when the vapor phase pitting is controlled). At very high temperatures (890°C) the refractory, Al_2O_3, and the cermet, LT-1, are corrosion-resistant. Alternately the melt could be heated internally as in a Kraft Recovery Furnace, and the high temperature melt could be contained in a frozen skull of the salt on cooled vessel walls.[15,16]

These results demonstrate adequate back-up materials or containment techniques in the event future corrosion tests or other considerations (such as design, procurement, fabrication, cost, or code) force the selection of alternate materials or containment methods. In addition, the screening tests have been broad enough in scope to predict the corrosion resistance of materials not tested.

V. RECOMMENDED MATERIALS FOR THE SMALL PILOT PLANT

Subject to the results of continuing corrosion tests, the following materials are recommended for use in the various portions of the small pilot plant (SPP). It should be emphasized that the choice of materials specified below is based on corrosion resistance, and that design, cost, fabrication, code, or procurement considerations may force the selection of alternate materials.

A. Absorption and Regeneration

Materials for the absorption and regeneration steps of the process will probably not be a problem, because of the low temperatures involved. These steps will be performed at 425-500°C. Our corrosion data indicate that even at 500°C, the iron-based alloy SS-347 will contain all melts satisfactorily. Therefore, this material is recommended for all the low temperature (500°C and below) components of the SPP.

B. Reduction

This step will be carried out at 600-650°C if hydrogen is used as the reducing agent or at 750-850°C if carbon is used as the reducing agent. Presently, carbon reduction with internal combustion to heat the melt and

maintain it at the reducing temperature is planned. Therefore, waterwall construction to contain the molten salt in a skull of frozen salt is recommended. Stainless steel 347 is recommended as the construction material for the waterwalls in the SPP although many Kraft Recovery Furnaces use carbon-steel tubes.

C. Back-Up Materials

A nickel-based alloy is recommended as the back-up material for SS 347. According to short-term tests, Hastelloy G is the most corrosion-resistant (< 5 mils/yr), easily fabricable, and readily available material. However, it is anticipated that Hastelloy B, C, N, X, Inconel 600, 702, or Haynes 25 would prove satisfactory below 500°C.

VI. FUTURE CORROSION TEST PROGRAM

Additional corrosion data required before Pilot Plant construction would be the corrosion rate of type 347 stainless steel as a function of time and melt content, i.e., sulfide, sulfite, nitrite, nitrate, chloride and other impurities, from 400 to 500°C. Other austenitic stainless steels will be studied in order to determine if 347 has significantly superior corrosion resistance to offset possible fabrication problems (i.e., under-bead cracking). Other high temperature materials (i.e., Ti and Ta), coatings (i.e., Rokide or NORCO), and alloys (such as Union Carbide Alloy 188) will be investigated. Thermal cycle and both thermal convection and pumped loop tests on austenitic stainless steels and nickel-based alloys will be performed. In addition, further screening tests will be conducted on promising materials (i.e., refractory oxides, etc.) and special tests will be conducted on materials (e.g., for pump impellers and bearings) as design and procurement considerations dictate.

Plastic chrome ore and other cold-wall lining materials will be studied as insulation in internally heated vessels where internal combustion raises the melt to the reducing temperature.

VII. CONCLUSIONS

These results show that at temperatures below 500°C, the niobium-stabilized stainless steel 347 has a linearly extrapolated corrosion rate of only a few mils/yr even in the most corrosive (sulfide) fused salt. At higher temperatures (600-650°C), the cobalt-based alloy Haynes 25 is satisfactorily corrosion resistant. At even higher temperatures (700°C), Uniloy is very corrosion resistant (when the vapor phase pitting is controlled). At very high temperatures (890°C) the refractory, Al_2O_3, and the cermet, LT-1, are corrosion resistant. Alternately internal heating with cold-wall containment can be used in the high temperature reduction step.

Therefore, it is recommended that SS 347 be used in the low temperature (absorber and regenerator) portion of the Small Pilot Plant and that cold-wall construction be used in the carbon reducer. In addition, long range corrosion studies are proposed in anticipation of Prototype Plant construction.

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